NEW FAILURE MECHANISM IN SILICON NITRIDE RESONATORS

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ABSTRACT

This study focuses on a new reliability problem of micromechanical structures based on thin silicon nitride films. Silicon nitride is used in numerous MEMS applications thanks to its good mechanical and electrical properties. The SiN_x micromechanical structures usually serve as supporting elements such as membranes, plates and cantilevers. A new failure mechanism is found in thin resonating SiN_x structures operating in air. The stiffness of the structure is changing due to surface oxidation. The surface oxide layer can crack and recover during operation of the device. This results in unstable resonance frequency and failure of the resonant mode MEMS device.

INTRODUCTION

The silicon nitride thin film used in MEMS is formed by low-pressure or plasma enhanced chemical vapor deposition (LPCVD, PECVD) and processed with standard micromachining techniques. The silicon nitride film has excellent mechanical, electrical and thermal properties for various applications. The main fields of applications are supporting mechanical elements, insulator layers, protective coatings. The first group is particularly interesting for micromachining. Extreme aspect ratio structures such as large membranes, plates or cantilevers are fabricated of thin silicon nitride film. Butler et al. built a flexural wave resonator based on a silicon nitride membrane [1]. They showed how sensitive the resonant device is for membrane stress. Stress is a main contributor to the resonance frequency. The environment, e.g. temperature, pressure, etc. can change the stress in the membrane and shift the resonance frequency. The environmental parameters can be measured this way. The LPCVD silicon nitride is usually in tensile stress on the silicon substrate. Large displacement enhances the membrane tension and leads to amplitude-induced stiffening. Heating the membrane reduces the tension and results in decreased resonance frequency. Hence the resonance frequency of the device can be tuned by controlling the internal stress. Lee and White used silicon nitride plate as voltage-to-frequency converter [2]. The resonance frequency was tuned with electrostatic field, statically deflecting the plate.

This study addresses a reliability problem, which leads to resonance frequency shift. Thin silicon nitride structures operating in air have unstable resonance frequency. The oxidation of the silicon nitride surface is responsible for this behavior. Marxer et al. found the same resonance frequency characteristic on thin polysilicon membrane [3]. The humid environment oxidized the surface increasing the stiffness and so the resonance frequency of the membrane. This mechanical drift results in failure of the resonant mode device. The surface oxidation generates high internal stress, and can lead to corrosion fatigue. No dislocation movement is present in polysilicon; therefore slow crack growth and rupture are initiated by the failure of the surface oxide layer. Connally and Brown came to the same conclusion while measuring the crack growth rate on precracked polysilicon samples [4]. The humidity enhanced the crack growth.

THEORY

The resonant method is a simple and accurate way to determine the Young's moduli of thin films. Monitoring the Young's modulus during accelerated aging and life cycling tests give information about the reliability and long term stability of the structure. The Young's modulus (E) can be calculated from the resonance frequency of a thin cantilever beam [5]. The resonance frequency is given by the following equation:

$$f_{res.} = \frac{A}{2p}\sqrt{\frac{EI}{r_L L^4}} \qquad (1)$$

where $f_{res.}$ = resonance frequency
E = Young's modulus
I = area moment of inertia of cross-section
L = beam length
r_L = mass per unit length of beam
A = a coefficient related to end conditions, A=3.52 for the first natural mode of a clamped – free cantilever.

The other characteristic factor of the resonator is the quality factor, which describes the coupling of input energy to the output resonance energy. The quality factor is mostly dependent on the damping of the environment. Acoustic radiation, internal friction and fatigue processes also lead to energy loss [6]. The quality factor is given by

$$Q = \frac{f_{res.}}{\Delta f_{FWHA}} \quad (2)$$

where $f_{res.}$ is the resonance frequency and Δf_{FWHA} is the full width at half amplitude of the resonance peak, the 3dB point.

The low-stress LPCVD silicon nitride film is a two component amorphous material, a mixture of Si and SiN_x clusters. The structural order is described with the radial distribution function [7]. The typical cluster size is 10 angstrom and the energetically most stable form of SiN_x is the Si_3N_4.

Environmental effects can change the properties of thin films. Silicon nitride is a chemically stable material, but the surface incorporates oxygen when exposed to air or water vapor. This results in increased surface conductivity [8] and in change of mechanical properties. The Si-N bond oxidize when subjected to air or water, and the reaction is described with the following equations [9]:

$$Si_3N_4(s) + 3\ O_2(g) \rightarrow 3\ SiO_2(s) + 2\ N_2(g) \quad (3)$$

$$\Delta F_{298°C} = -304 \text{ kcal/mole}$$

$$Si_3N_4(s) + 6H_2O(g) \rightarrow 3\ SiO_2(s) + 4\ NH_3(g) \quad (4)$$

$$\Delta_{F298°C} = -147 \text{ kcal/mole}$$

where ΔF is the free-energy change of the reaction. The surface oxidation of silicon nitride at room temperature is thermodynamically feasible. The Si atoms at the surface bond to the more electronegative O atoms instead of the N atoms. Raider et al. examined the surface oxidation of silicon nitride at room temperature and at elevated temperature with x-ray photoelectron spectroscopy (ESCA) [9]. The silicon nitride is rapidly oxidized in air at room temperature. The oxidant can be water vapor or oxygen, but their relative reactivity is not known. The surface of silicon nitride is likely to be a graded oxynitride, which is oxygen rich and nitrogen deficient at the film surface. The O is chemically bound to the Si. The silazane (Si-N-Si) bridge of silicon nitride is changed to siloxane (Si-O-Si), which is present in silicon oxynitride films. According to the ESCA measurements, the formed SiO_xN_y is not a mixture of SiO_2 and Si_3N_4 clusters, but the siloxane and silazane groups are blended on the molecular scale. On elevated temperatures first oxynitride, than later SiO_2 is formed on the silicon nitride surface.

EXPERIMENTAL

Sample preparation

The silicon nitride samples were fabricated in Delft Institute for Microelectronics and Submicron Technology (DIMES). Cantilever beams with different shape and size were patterned in low-stress silicon rich silicon nitride film, see Figure 1.

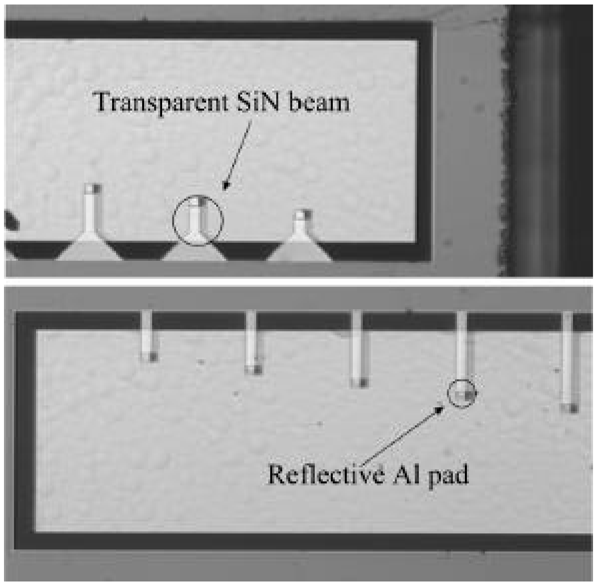

Figure 1. Optical microscope picture of the SiN_x cantilever beams

The SiN_x film was deposited from dichlorosilane (DCS) and ammonia (NH_3) gases with LPCVD. French and Sarro studied the deposition conditions in order to achieve low-stress silicon nitride films [10]. Based on their results a gas-flow ratio of NH_3/DCS=0.176, deposition pressure of 150mtorr and deposition temperature of 850°C were used. The Si/N ratio is 0.95 in the film, there is no detectable hydrogen content, and the residual tensile stress is 0.125GPa. X-ray diffraction studies proved that the SiN_x film is amorphous. The patterned SiN_x cantilevers were etched free with topside wet etching in 25% 80°C TMAH. Aluminum pads were deposited on the free end of the beam for optical readout technique. The aluminum was protected during etching with a silicon oxide layer, which was removed with HF. Finally the chips were diced while the cantilevers were protected with a thick resist layer filling up completely the well under the beams. The resist was removed with acetone. The cantilever beams are 0.32μm thick, 15-40μm wide and 85-325μm long. The dimensions are checked with scanning electron microscope (SEM). The uniformity of the thickness is better than 5nm at different positions of the wafer. There is a 1-2μm wide undercut at the clamping of the beams as the silicon is etched slowly in the (111)-direction as well. The width of the undercut region depends on the etching time.

Finite element simulations (FEA) showed that the resonance frequency of an undercut beam agrees to a close approximation with the resonant frequency of an ideally clamped but longer beam. This approximation holds for the first resonance mode of all the used beams. Therefore the effective length of the beam is the designed length plus the undercut width.

Measurements

We used the resonant method to characterize and monitor mechanical properties of silicon nitride films. Optical readout technique was implemented to achieve high measurement accuracy. Using external mechanical excitation allows us to keep the samples simple, hence providing easier evaluation of the measurement results. To combine optical readout and external mechanical driving techniques, atomic force microscopy (AFM) was implemented [11]. Park Scientific Instruments' AutoProbe M5 and Digital Instruments' MultiMode SPM was used in this study. The sample cantilever beam is mounted in the AFM head. The cantilever is excited mechanically with a sweep, while the deflection of the free end is measured continuously with a bouncing laser beam, see Figure 2. The measured peak gives the resonant frequency of the cantilever beam. The typical excitation amplitude of the sweep is a few nanometers. The maximum displacement of the cantilever's free end in resonance is 4-5 times bigger than the excitation amplitude. This few nanometer deflection is in the elastic range, as the thickness of the cantilever is 320nm. Note that the thin silicon nitride cantilevers are so flexible, that a 100μm long cantilever can bend 50 microns easily with no visible change at all. The resonant AFM technique provides very high accuracy and measurement reproducibility of 10Hz. The Young's modulus can be calculated from the resonant frequency of the beam. The accuracy of the method is limited by the measurement accuracy of the length, thickness and mass density of the sample. The effect of air damping on the resonance frequency can be neglected, but determines the quality factor [12].

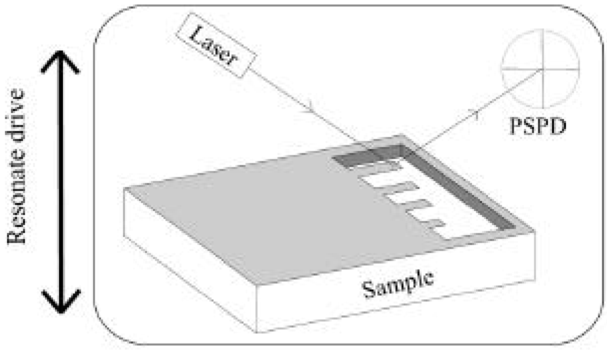

Figure 2. Resonance frequency measurement of cantilevers in the AFM head

The resonant method can be applied as life-cycling test, in which the beam is driven in resonance for long time. The excitation amplitude can be set in the AFM. The resonant frequency is measured frequently during the test. The 10Hz measurement accuracy corresponds to less than 0.03% inaccuracy in case of our samples. This means that the change of mechanical properties e.g. microcrack generation can be monitored with high accuracy by measuring the shift of the resonance frequency. The dimensions and other parameters remain constant during the tests. Consequently the change of Young's modulus due to aging or life cycling can be measured with much higher accuracy, than the absolute value.

RESULTS AND DISCUSSION

Young's modulus of 230±11GPa was calculated for silicon nitride from the AFM resonant measurements [13]. This result was verified with finite element simulations (FEA). Note that E from 95 to 320GPa were presented in the literature for low-stress LPCVD SiN. The quality factor was 50±10 calculated from the measured peak. This value agrees with analytical calculations based on viscous air damping theory.

The long-term stability of micromechanical structures can be described with the stability of the resonance frequency. The cantilevers were driven in resonance in air for a long period and the resonance frequency was measured frequently. The stiffness of the samples increased in time and the resonance frequency increased accordingly [13], see Figure 3. The same stiffening behavior was obtained on samples, which were swept only during the resonance frequency measurements, otherwise stood still in air.

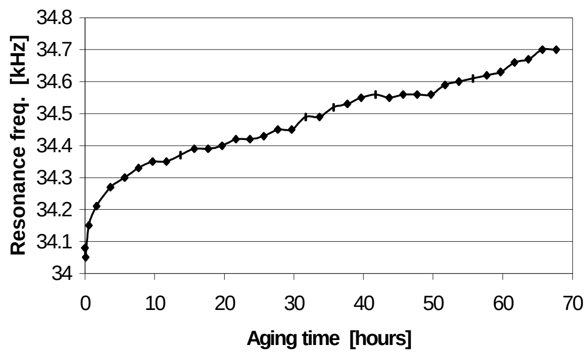

Figure 3. Stiffening effect on SiN_x cantilever operating in air

The oxidation of the silicon nitride film surface leads to the measured stiffening effect. The formed oxynitride is in strong compressive stress stretching the nitride film. The result is a multilayer structure with internal stresses. As stress is a major contributor to the resonance frequency, the introduced tensile stress in the cantilever results in higher resonance frequency. The stiffening effect is strongly dependent on the film thickness. It is likely to be the reason, that others [1, 2] did not find this phenomena before on 1-2 micrometer thick silicon nitride membranes, while similar stiffening effect was reported on thin polysilicon membrane [3].

The silicon nitride cantilevers were subjected to mechanical shock and large deflection. The AFM's built-in piezoelectric actuator applied the mechanical shock to the sample. The large deflection was realized by resonant driving at higher excitation amplitudes or externally by another AFM cantilever explained elsewhere [13]. The shock and the deflection generates an abrupt drop in the resonance frequency, see Figure 4. The height of the frequency step depends on the magnitude of the shock or large deflection. Afterwards the resonance frequency increases fast in the beginning, then linearly.

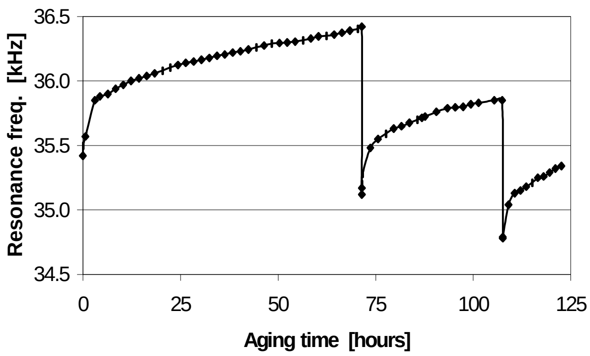

Figure 4. Shock and large deflection generates a negative step in the resonance frequency.

This unstable behavior of the resonance frequency can be explained with the surface oxidation theory. The shock or large deflection damages the oxynitride layer. The discontinuities on the surface layer weaken the stiffening effect, so the overall stiffness of the structure drops. After the applied shock or deflection, the surface re-oxidizes hence the stiffness and the resonance frequency increase again. It is not clear what damage is formed on the surface due to the mechanical shock, but generation and propagation of cracks are likely to occur. Surface microcracks at the clamping are observed with the AFM on the silicon nitride samples, see Figure 5.

To confirm the surface oxidation theory, repeated resonant tests were conducted in various environments. Air, humidity, nitrogen and argon have different influence on the stiffening effect. The AFM was operating in an environmental chamber. Large deflections of 20-30nm were applied to the samples with 5sec long high amplitude resonant driving. Then the change of the resonance frequency was measured in every 30 second for 2.5 minutes. The tests were repeated in every 3 minutes. Note that this large deflection is still in the elastic range of the silicon nitride beams. "Large" indicates that the deflection is approximately 10 times bigger than the one used in the resonance frequency measurements. This large deflection generates only a small negative step in the resonance frequency, which totally recovers in 2 minutes, unlike the large deflections and shocks applied in Figure 4. The first few large deflection tests show hysteresis. Here the deflection results in higher resonance frequency drop, which does not recover fully in a few minutes. This is due to the cracking of the thicker oxynitride layer, which grew earlier on the samples in air. Then the sample reaches dynamic balance with the environment, where the repeated large deflection tests are reproducible within 20%. The results of 5-10 tests are averaged and the mean resonance frequency shift values are plotted vs. time on the following figures.

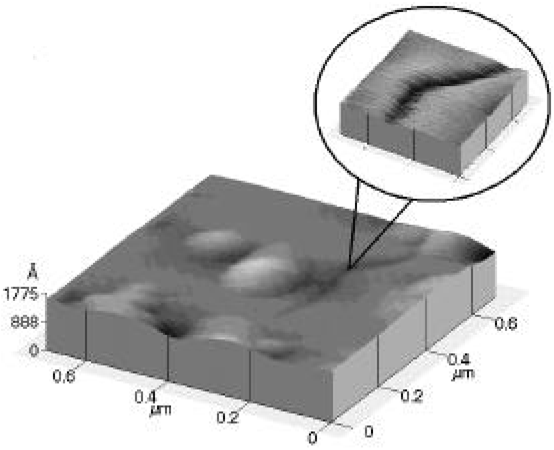

Figure 5. AFM image of a microcrack on the cantilever surface generated by mechanical shock.

The crack generation and healing processes were compared in air and in nitrogen rich environments, see Figure 6. In air, the cracks generated after the large deflection all healed within 2 minutes. The resulting resonance frequency is higher then the initial due to the stiffening effect. The same tests were repeated in nitrogen rich environment. The average resonance frequency is lower, 30kHz instead of the 31kHz measured in air. The resonance peak is narrower; hence the quality factor of the resonating cantilever is higher. The recovery of the resonance frequency after the large deflections is much slower than in air, and the resonance frequency after 2.5 minutes is lower than the initial. The lower oxygen and water vapor content of the silicon rich environment explains this behavior, as the surface oxidation process is slower here. Further increased nitrogen content led to yet weaker resonance frequency recovery effect. The negative shift of the resonance frequency is also lower in nitrogen rich environment. As the resonance frequency does not recover fully during the 3 minutes break between the tests, the oxynitride film remains damaged. Consequently the same large deflection can not create such a resonance frequency drop as in air.

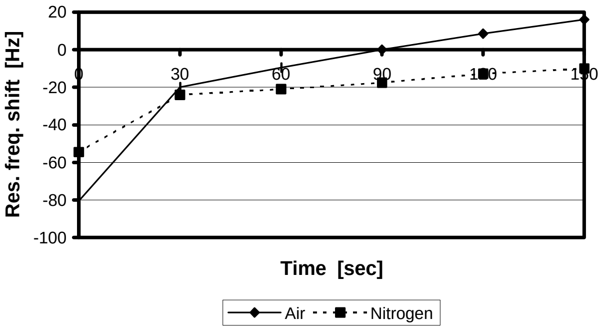

Figure 6. Large deflection tests in air and in nitrogen rich environment

The nitrogen atmosphere is inert in respect of the surface oxidation, but it might interact with the silicon nitride surface changing the mechanical properties of the cantilever. To eliminate this possible effect, large deflection tests were conducted in argon rich environment and compared to tests in air, see Figure 7. The crack healing and the stiffening of the cantilever are slower than in air, and the negative frequency shift due to the large deflection is smaller as well. This behavior is identical with the measurements in nitrogen rich environment and therefore explained in the previous paragraph.

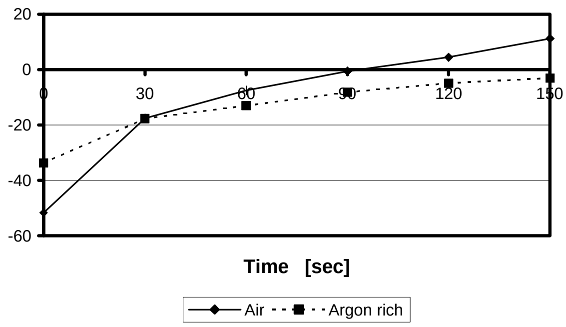

Figure 7. Large deflection tests in air and in argon rich environment

If the surface oxidation theory holds for the stiffening effect of thin silicon nitride cantilevers in air, than humid environment have to enhance the stiffening. The large deflection tests were repeated in air with increased humidity. The oxygen and the water vapor both lead to formation of oxynitride on the surface of silicon nitride [9]. Humidity proved to have the opposite effect on stiffening than nitrogen and argon rich environments, see Figure 8. The stiffening effect is stronger than in air. The responding resonance frequency drop is higher, and the following recovery of the frequency is faster than in air. These enhanced effects are explained with the higher content of oxidants (oxygen gas and water vapor). The oxynitride is thicker on the silicon nitride surface, and the crack healing process is faster. The resonance peak widens and shifts to higher values in seconds when the sample is introduced to the humid environment. This indicates that surface oxidation takes place fast. This agrees with the fast crack healing process, where the microcracks initiated by the large deflection are re-oxidized in a few minutes. If the humidity is further increased, the response curve becomes noisier and the resonance peak becomes yet wider.

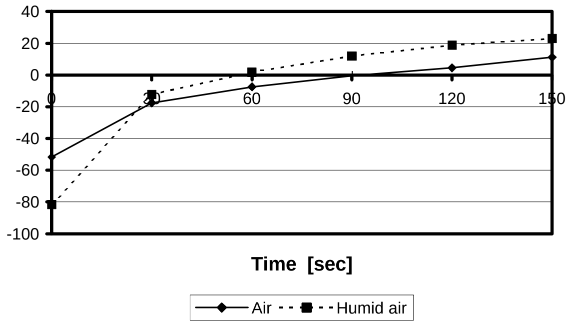

Figure 8. Large deflection tests in air and in humid environment

CONCLUSIONS

Silicon nitride thin films find more and more potential applications in MEMS devices as structural element, thanks to its good mechanical properties. We found a new failure mechanism of resonant SiN_x devices operating in air, which we have already reported elsewhere [13]. The resonance frequency becomes unstable, which leads to failure of resonant mode devices. In this study the degradation process is further characterized, and an explanation is given to the unstable behavior.

Low-stress LPCVD silicon nitride was characterized using the resonant AFM method. Young's modulus of 230±11GPa was calculated from the resonance frequency. The thin silicon nitride cantilevers showed a stiffening effect in air, the resonance frequency increased gradually. When the cantilever is subjected to mechanical shock or large deflection, the resonance frequency suddenly drops, and then increases again. This behavior can be explained with oxidation of the cantilever surface. The silicon nitride tends to oxidize in air at room temperature forming a graded oxynitride layer on the surface. The oxynitride layer introduces internal stress in the cantilever increasing the overall stiffness of the structure. The surface oxynitride layer cracks due to shock or large deflection. The damage of the oxynitride layer weakens the stiffening effect hence the resonance frequency drops. As the surface re-oxidizes after the shock in air, the stiffness and consequently the resonance frequency increase again. Repeated large deflection tests were conducted in various environments. Nitrogen and argon rich environments decreased the stiffening effect of the thin silicon nitride cantilever. The crack healing process, which follows the large deflections, is slower as well. Nitrogen and argon both proved to be inert in respect of the surface oxidation process, and could be used potentially in sensor packaging. Humid environment has the opposite influence; the oxidation of the silicon nitride surface is enhanced. Consequently the stiffening and the crack healing effects are stronger, as indicated by the shift of resonance frequency. The tests in different environments supported the surface oxidation theory, which describes the unstable behavior of resonance frequency.

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